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Synthesis of metallacyclobutanes and metallacyclobutabenzenes of molybdenum and tungsten

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Abstract

Reactions of 1,3-bis(bromomagnesio)-2,2-dimethylpropane or 1-magnesacyclobutabenzene with either dichloromolybdenocene or dichlorotungstenocene have given the corresponding four-membered metallacycles of both metals.

Introduction

Molybdena- and tungstena-cyclobutanes have been prepared by nucleophilic attack on η^3-allyl complexes [1–4], and tungstenacyclobutanes have also been obtained by [2 + 2] addition of alkenes to a carbenetungsten complex [5]. In continuation of our exploration of the use of 1,3-divalent organomagnesium or organolithium reagents for the synthesis of four-membered metallacycles [6], we have treated 1,3-bis(bromomagnesio)-2,2-dimethylpropane (**1**) [7,8] and 1-magnesacyclobutabenzene (**2**) [9,10] with dichloromolybdenocene (**3a**) or with dichlorotungstenocene (**3b**) (Scheme 1).

Results and discussion

Metallacyclobutanes of Mo and W

As molybdena- and tungstena-cyclopentanes could not be isolated from the reaction of the corresponding dichlorometallocenes and 1,4-bis(bromomagnesio)butane in diethyl ether [11], we had reason to expect similar problems, and indeed, when compound **1** was treated with equimolar amounts of **3a** or **3b** in diethyl ether at room temperature for 6 h, unchanged starting materials were left in significant amounts. However, when the reactions were performed in tetrahydrofuran and the mixture was stirred for 3 h at room temperature in the case of **3a** or for 12 h at 50 °C in the case of **3b**, the desired metallacyclobutanes **4a** and **4b** were isolated after work-up as crystalline materials in 80 and 18% yields, respectively. Products **4a** and **4b** were identified by ^{1}H and ^{13}C NMR spectroscopy; the ^{1}H NMR spectra were in accordance with those reported for similar compounds [1–4]. Because of the

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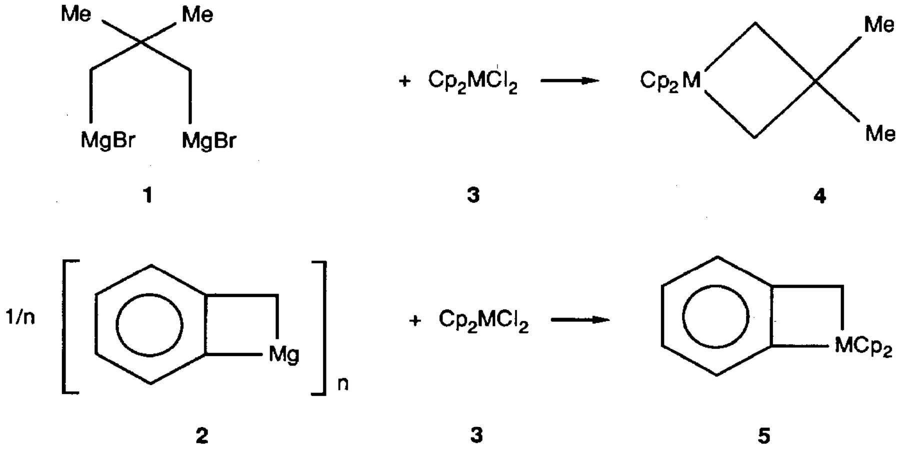

Scheme 1. **a**: M = Mo; **b**: M = W.

low yield of **4b**, efforts were made to identify the by-products, but these were unsuccessful.

Molybdenacyclobutanes do not readily dissociate into an alkene and a metal-carbene complex [3,4], and so it was not surprising that **4a** did not react with cyclohexanone even after long periods at elevated temperatures. In contrast to four-membered titanacycles [6,12,13], **4a** was recovered unchanged after treatment with chlorotrimethylstannane or trimethylphosphine. Although alkylmolybdenum compounds normally react with iodine to give the corresponding iodoalkane and molybdenum iodide in quantitative yield [14], **4a** gave 1,1-dimethylcyclopropane (67%) and 1,3-diiodo-2,2-dimethylpropane (17%).

Metallacyclobutabenzenes of Mo and W

When a suspension of **2** in tetrahydrofuran was treated with **3a** or **3b** at room temperature, **5a** and **5b** were isolated as orange solids in 11 and 16% yield, respectively. The new compounds were identified by ^{1}H and ^{13}C NMR spectrometry; the benzylic protons and the benzylic carbon are more shielded than those in 1,1-dicyclopentadienyl-1-titanacyclobutabenzene ($\delta(CH_2)$ 3.30; $\delta(CH_2)$ 63.4 ppm [15]). This effect is also observed for the α-position in the metallacyclobutane series (this work and ref. [6]).

The low yields of both **5a** and **5b** were disappointing; the by-products could not be isolated or identified, but they are probably higher condensation products which would not be unexpected from reactions involving combination of two divalent reaction partners [9]. At room temperature, the metallacyclobutabenzenes were stable in solution. After one month, in each case only 10% had decomposed, to give toluene and an organometallic product that could not be identified. The reactivities of **5a** and **5b** are being investigated.

Experimental

Solvents were distilled from sodium potassium alloy. The di-Grignard reagents **1** [7,8] and **2** [9,10], dichloromolybdenocene [16] and dichlorotungstenocene [17] were prepared by literature procedures. All experiments were performed in a completely sealed and evacuated glass apparatus [18]. ^{1}H NMR spectra were recorded on a Bruker WH 90 or a Bruker WM 250 spectrometer, operating at 90 MHz or 250 MHz, respectively; ^{13}C NMR spectra were recorded on a Bruker WM 250, operating at 63 MHz. High resolution mass measurements were performed with a Varian MAT CH5 DF mass spectrometer, operating at an ionization potential of 70 eV. The ions containing molybdenum showed the expected isotope pattern. Yields were determined by quantitative ^{1}H NMR spectroscopy (internal standard: cyclopentane or hexamethylbenzene). Microanalyses were performed at the Rijksuniversiteit Groningen, The Netherlands, under the supervision of Mr. A.F. Hamminga.

*1,1-Dicyclopentadienyl-3,3-dimethyl-1-molybdenacyclobutane (**4a**)*

A solution of 0.071 mmol of **1** in 10 ml of diethyl ether was added at room temperature to 0.071 mmol of **3a** (21.0 mg). The diethyl ether was evaporated off and 10 ml of tetrahydrofuran were added to the residue. The mixture was stirred for 3 h at room temperature and dioxane (3 ml) was added, to give a white precipitate and a red brown solution. The solution was filtered and the filtrate evaporated to leave crude **4a** (80%, ^{1}H NMR), which was sublimed (0.0001 mb, 50 °C) to give orange red crystals. ^{1}H NMR (90 MHz, C_6D_6): δ 0.65 (s, 4H), 1.19 (s, 6H), 4.34 ppm (s, 10H). ^{13}C NMR (63 MHz, C_6D_6): δ -6.1 (t, ^{1}J(CH) 131 Hz), 36.8 (q, ^{1}J(CH) 123 Hz), 49.7 (s), 86.6 ppm (d, ^{1}J(CH) 178 Hz). Found: C, 59,63; H, 6.68. $C_{15}H_{20}Mo$ calc.: C, 60.81; H, 6.81%.

*1,1-Dicyclopentadienyl-3,3-dimethyl-1-tungstenacyclobutane (**4b**)*

The reaction involving **1** and **3b** was carried out as described for preparation of **4a**, except that the reaction mixture was stirred for 12 h at 50 °C (yield of **4b**: 18%). After sublimation (0.0001 mb, 80 °C), **4b** was isolated as yellow orange crystals. ^{1}H NMR (90 MHz, C_6D_6): δ 0.93 (s, 4H, ^{2}J(WH) 9 Hz), 1.05 (s, 6H), 4.27 ppm (s, 10H). ^{13}C NMR (63 MHz, C_6D_6): δ -20.4 (t, ^{1}J(CH) 130 Hz, ^{1}J(WC) 45 Hz), 37.4 (q, ^{1}J(CH) 122 Hz), 51.1 (s), 83.4 ppm (d, ^{1}J(CH) 180 Hz). Found: C, 46.76; H, 5.07. $C_{15}H_{20}W$ calc.: C, 46.89; H, 5.25%.

*1,1-Dicyclopentadienyl-1-molybdenacyclobutabenzene (**5a**)*

To 0.34 mmol of **3a** (100.6 mg) was added a suspension of 0.34 mmol of **2** in 80 ml of tetrahydrofuran. The mixture was stirred for 3 h at room temperature, then the solvent was evaporated off and 15 ml of n-pentane added to the brown residue; this led to formation of a yellow solution and a dark brown residue. The solution was filtered and the filtrate evaporated to leave **5a** as an orange solid; yield: 11.9 mg (11%). ^{1}H NMR (250 MHz, C_6D_6): δ 1.53 (s, 2H), 4.25 (s, 10H), 6.51 (d, ^{3}J(HH) 7 Hz, 1H), 7.05 (m, 2H), 7.52 ppm (d, ^{3}J(HH) 7 Hz, 1H). ^{13}C NMR (63 MHz, C_6D_6): δ 30.6, 87.4, 123.9, 125.5, 125.6, 137.2, 139.7, 164.1 ppm. HRMS: found 318.0366, $C_{17}H_{16}{}^{98}Mo$ calc. 318.0307.

*1,1-Dicyclopentadienyl-1-tungstenacyclobutabenzene (**5b**)*

The synthesis of **5b** was performed as described above for **5a** except that the mixture of **2** and **3b** was stirred for 6 h at room temperature; **5b** was isolated as an orange solid. Yield: 22.0 mg (16%). ^{1}H NMR (250 MHz, C_6D_6); δ 1.77 (s, 2H, ^{2}J(WH) 2 Hz), 4.37 (s, 10H), 6.89 (m, 1H), 7.08 (m, 2H), 7.34 ppm (m, 1H). ^{13}C

NMR (63 MHz, C_6D_6): δ 35.7, 83.6, 121.0, 123.6, 123.7, 134.2, 138.1, 144.2 ppm. Attempts to measure a mass spectrum by direct inlet and electron impact were unsuccessful.

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